

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-165701

(43)Date of publication of application : 10.06.2003

(51)Int.Cl. C01B 3/00
B01J 20/02
C01B 31/04

(21)Application number : 2001-361155 (71)Applicant : TOYOTA CENTRAL RES & DEV LAB INC

(22)Date of filing : 27.11.2001 (72)Inventor : WAKAYAMA HIROAKI
FUKUSHIMA YOSHIKI

(54) HYDROGEN STORAGE MATERIAL AND METHOD OF MANUFACTURING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage material which releases high-purity hydrogen and in addition, enough quantity of hydrogen at a low temperature.
SOLUTION: The hydrogen storage material is characterized by containing at least one kind of catalyst selected from the group consisting of nickel, chromium, molybdenum, cobalt, copper, palladium, platinum, iron, ruthenium, rhodium, iridium, tungsten, titanium, manganese and osmium, and carbon.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

BEST AVAILABLE COPY

[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] The hydrogen absorption ingredient characterized by containing at least one sort of catalysts chosen from the group which consists of nickel, chromium, molybdenum, cobalt, copper, palladium, platinum, iron, a ruthenium, a rhodium, iridium, a tungsten, titanium, manganese, and an osmium, and carbon.

[Claim 2] As a raw material of said carbon, the Raman full width at half maximum of wave number 1350cm^{-1} obtained by Raman spectrum measurement is following type (1): $d < (376/La) + 19.0$. (1)

It is the hydrogen absorption ingredient according to claim 1 characterized by being the thing which comes to blend the graphite crystal grain child who fulfills the conditions expressed with [d expresses the Raman full width at half maximum (cm^{-1}) among a formula, and La expresses the crystal grain child size within the field containing the a-axis and b-axis of graphite structure (nm)].

[Claim 3] The hydrogen absorption ingredient according to claim 1 or 2 with which the content rate of said carbon is characterized by being more than 40 atom % on the basis of the total quantity of said catalyst and said carbon.

[Claim 4] With the grinding process which obtains a graphite crystal grain child by mechanical grinding of a graphite, and the graphite crystal grain child obtained at said grinding process At least one sort of catalysts chosen from the group which consists of nickel, chromium, molybdenum, cobalt, copper, palladium, platinum, iron, a ruthenium, a rhodium, iridium, a tungsten, titanium, manganese, and an osmium are mixed. The manufacture approach of the hydrogen absorption ingredient characterized by including the mixed process which obtains the hydrogen absorption ingredient containing this catalyst and carbon.

[Claim 5] The manufacture approach of the hydrogen absorption ingredient according to claim 4 characterized by including further hydrogen down stream processing which contacts said hydrogen absorption ingredient in hydrogen.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a hydrogen absorption ingredient and its manufacture approach.

[0002]

[Description of the Prior Art] In modern society, hydrogen is an important chemistry raw material used for synthetic chemistry industry, petroleum refining, etc. so much. On the other hand, in order to solve energy problems and the environmental problem in the future, it is thought that the hydrogen use technique as clean energy occupies an

important location, hydrogen is stored, and development of the fuel cell which works considering it as a fuel is furthered.

[0003] This fuel cell is a cell which operates by gas, and transforms into direct electrical energy the energy obtained from the reaction of hydrogen and oxygen in that case. Since such a fuel cell has very high effectiveness compared with the conventional combustion engine and does not have emission of toxic gases, such as NO_x, SO_x, and CO, the automobile which has a fuel cell is called ZEV (Zero Emission Vehicle).

[0004] The approach of compressing and on the other hand, storing in a bomb as preservation of hydrogen, the approach of cooling and making it into liquid hydrogen, the method of making it stick to activated carbon, the method of using a hydrogen absorption ingredient, etc. are proposed. It is thought that the method of using a hydrogen absorption ingredient plays main roles in migration media, such as a fuel cell powered vehicle, also in these approaches.

[0005] Use of the carbon as a hydrogen absorption ingredient is proposed under such a background (the Patent Publication Heisei No. 504394 [eight to] official report, JP,2000-103612,A, JP,2001-106516,A, etc.). Moreover, the hydrogen absorption ingredient which mixed carbon to the alkaline earth metal (Mg, calcium, etc.) with which examination is conventionally advanced as a hydrogen absorption ingredient is indicated by JP,2000-87172,A, and improvement in the hydrogenation rate of alkaline earth metal is achieved by mixing with this alkaline earth metal and carbon. Furthermore, in case the hydrogen absorption ingredient which consists of Mg and graphite is manufactured, the method of performing mechanical grinding under coexistence (THF etc.) of a specific organic compound for the purpose of improvement in the property of the hydrogen absorption ingredient obtained is proposed (J.Alloys.Comp.293-295 (1999) p564-568, Chem.Comm.(1999) p2277-2278, etc.).

[0006]

[Problem(s) to be Solved by the Invention] However, even if it is the above-mentioned conventional hydrogen absorption ingredient, it is hard to say that there are not necessarily many hydrogen storage capacities per unit weight, and it has sufficient hydrogen absorption and emission ability in respect of utilization. Moreover, although a hydrogen absorption ingredient is expected to be able to perform occlusion and emission of hydrogen reversibly at low temperature (preferably room temperature), in order to make hydrogen emit from the above-mentioned conventional hydrogen absorption ingredient, it is necessary to heat to an elevated temperature (for example, 500 degrees C or more), and it becomes easy to mix a hydrocarbon (HC) into the hydrogen emitted by this heating, and the purity of hydrogen becomes inadequate.

[0007] This invention is made in view of the technical problem which the above-mentioned conventional technique has, and aims at offering the hydrogen absorption ingredient which can emit the hydrogen of a high grade and sufficient amount at low temperature.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the hydrogen absorption ingredient of this invention is characterized by containing at least one sort of catalysts chosen from the group which consists of nickel, chromium, molybdenum, cobalt, copper, palladium, platinum, iron, a ruthenium, a rhodium, iridium, a tungsten, titanium, manganese, and an osmium, and carbon.

[0009] With the hydrogen absorption ingredient of this invention, since the reversible reaction of the occlusion and emission of hydrogen is fully promoted by the synergistic effect of the hydrogen absorption and emission ability which carbon has essentially, and a desorption operation of the hydrogen by the above-mentioned specific catalyst, it enables it to emit the hydrogen of a high grade and sufficient amount at low temperature.

[0010] Moreover, for the hydrogen absorption ingredient of this invention, the Raman full width at half maximum of wave number 1350cm^{-1} obtained by Raman spectrum measurement is following type (1): $d < (376/La) + 19.0$ as a carbonaceous raw material. (1) It is desirable that it is the thing which comes to blend the graphite crystal grain child who fulfills the conditions expressed with [d expresses the Raman full width at half maximum (cm^{-1}) among a formula, and La expresses the crystal grain child size within the field containing the a-axis and b-axis of graphite structure (nm)]. If the graphite crystal grain child who fulfills the above-mentioned specific conditions is blended with a catalyst, since the above-mentioned synergistic effect will be heightened more by the improvement in the distributed homogeneity of a catalyst and carbon, the hydrogen absorption ingredient which has more excellent hydrogen absorption and emission ability is realized.

[0011] Moreover, in the hydrogen absorption ingredient of this invention, it is desirable that a carbonaceous content rate is more than 40 atom % on the basis of the total quantity of a catalyst and carbon. It is in the inclination hydrogen absorption and whose emission ability improve more that a carbonaceous content rate is more than 40 atom %.

[0012] Moreover, the grinding process from which the manufacture approach of the hydrogen absorption ingredient of this invention obtains a graphite crystal grain child by mechanical grinding of a graphite, The graphite crystal grain child obtained at a grinding process, nickel and chromium, molybdenum, At least one sort of catalysts chosen from the group which consists of cobalt, copper, palladium, platinum, iron, a ruthenium, a rhodium, iridium, a tungsten, titanium, manganese, and an osmium are mixed. It is characterized by including the mixed process which obtains the hydrogen absorption ingredient containing this catalyst and carbon.

[0013] According to the manufacture approach of this invention, a graphite crystal grain child detailed [particle diameter] and uniform is obtained according to this grinding process. The hydrogen absorption ingredient of this invention which is excellent in hydrogen absorption and emission ability can be obtained efficiently and certainly by using this graphite crystal grain child as a carbonaceous raw material, and mixing this with the above-mentioned specific catalyst.

[0014] As for the manufacture approach of this invention, it is desirable that hydrogen down stream processing which contacts a hydrogen absorption ingredient in hydrogen is included further. In having the active spot where the carbon contained in a hydrogen absorption ingredient causes irreversible reaction, there is a possibility that the hydrogen by which occlusion was once carried out may become that it is hard to be emitted at low temperature, but since termination of the active spot concerned is carried out and it is inactivated from hydrogen by performing this hydrogen down stream processing, the facilitatory effect of a reversible reaction (occlusion and emission of hydrogen) can be heightened more.

[0015]

[Embodiment of the Invention] Hereafter, the suitable operation gestalt of this invention

is explained to a detail.

[0016] The catalysts contained into the hydrogen absorption ingredient of this invention are nickel (nickel), chromium (Cr), molybdenum (Mo), cobalt (Co), copper (Cu), palladium (Pd), platinum (Pt), iron (Fe), a ruthenium (Ru), a rhodium (Rh), iridium (Ir), a tungsten (W), titanium (Ti), manganese (Mn), or the osmiums (Os) as above-mentioned. A desorption operation of hydrogen high enough can be acquired by using these catalysts. One sort may be independently used for these catalysts, and they may combine two or more sorts.

[0017] Although especially the configuration of the catalyst concerned is not restricted, as for the mean particle diameter, it is desirable that it is 10 micrometers or less. Since the contacting efficiency of the catalyst concerned and carbon increases when mean particle diameter uses a catalyst 10 micrometers or less, carbon can heighten more the synergistic effect of the hydrogen absorption emission ability and the dehydrogenation operation of a catalyst which it has essentially.

[0018] The hydrogen absorption ingredient of this invention is constituted including an above-mentioned catalyst and carbon. It is desirable to use graphites (graphite), such as a natural graphite with high purity and a high artificial graphite of a degree of graphitization like your kind consideration tropism pyrolytic graphite (HOPG), as a raw material of this carbon.

[0019] Drawing 1 is the explanatory view showing typically a graphite crystal grain child's example used by this invention. In drawing 1, the carbon layer 1 which has the almost same configuration and area carries out a laminating to the shape of a column, and the crystal grain child of graphite structure is constituted. Moreover, the crystal grain child size (crystal particle diameter in a direction level to the field of the carbon layer 1) within the field where L_a [nm] contains the a-axis and b-axis of graphite structure, and L_c [nm] express the crystal grain child size (thickness in which the carbon layer 1 is piled up) of the direction of a c-axis of graphite structure among drawing 1.

[0020] Raman full-width-at-half-maximum d of wave number 1350cm^{-1} and the crystal grain child size L_a desirable [as the graphite crystal particle concerned / what has high crystallinity and the high homogeneity of crystal particle diameter] and specifically obtained by Raman spectrum measurement are following type (1): $d < (376/L_a) + 19.0$. (1) It is desirable to use the graphite crystal grain child who comes out and fulfills the conditions expressed. The relation of d and L_a which are expressed with the above-mentioned formula (1) is carbonaceous crystallinity and the homogeneous index of crystal particle diameter, and when d and L_a do not fulfill the above-mentioned conditions, it is in the inclination for crystallinity and the homogeneity of crystal particle diameter to become for it to be low and inadequate [hydrogen absorption and emission ability]. Moreover, half-value width d and the crystal grain child size L_a are following type (2): $d < (341/L_a) + 10.5$ by the same reason as the above. (2)

It is more desirable to use the graphite crystal grain child who comes out and fulfills the conditions expressed.

[0021] Moreover, in the graphite crystal grain child concerned, it is desirable that the crystal grain child size L_a is 4.0nm or less. It is in the inclination for the hole produced among crystal grain children as L_a is 4.0nm or less to increase, and for hydrogen absorption and emission ability to be raised more.

[0022] Moreover, the die length of a ***** of stratification plane inboard (direction

level to the field containing the a-axis and b-axis of graphite structure) is fully desirable, and, as for the graphite crystal grain child concerned, specifically, it is desirable that the ratio (L_a/L_c) of crystal grain child size is 0.15 or more. Furthermore, as for the specific surface area of a graphite particle, it is desirable that it is more than 100m²/g. Thereby, the hole produced on the front face of a graphite microcrystal can be made to increase. [0023] Moreover, as for the ratio (H/C) of the atomic number of carbon and hydrogen, in the graphite crystal grain child concerned, it is desirable that it is 0.05 or less. Formation of a hydroxyl group [in / that H/C is 0.05 or less / a crystal grain child's end], a carboxyl group, etc. is controlled.

[0024] In the hydrogen absorption ingredient of this invention, if contact to a catalyst and carbon is enough, especially these distributed conditions will not be restricted. For example, you may be any in the condition which the catalyst particle and the graphite crystal grain child are distributing minutely, the condition that the catalyst particle was introduced and the intercalation compound was formed between the layers of a graphite crystal grain child's carbon layer, or the condition that the catalyst particle was supported by the graphite crystal grain child front face. Moreover, when the graphite crystal grain child who fulfills the conditions expressed with the above-mentioned formula (1), for example as a carbon raw material is used, the graphite particle concerned may be distributed in the condition of not fulfilling the conditions expressed with a formula (1) in a hydrogen absorption ingredient.

[0025] Moreover, although a catalyst and a carbonaceous content rate are not restricted especially as long as sufficient hydrogen absorption and emission ability are obtained, it is desirable that a carbonaceous content rate is more than 40 atom % on the basis of the total quantity of a catalyst and carbon. It is in the inclination for hydrogen absorption and emission ability to fall that a carbonaceous content rate is under 40 atom %.

[0026] Thus, the hydrogen absorption ingredient of this invention contains the catalyst and carbon of the above-mentioned specification, and since the reversible reaction of the occlusion and emission of hydrogen is fully promoted by the synergistic effect with a desorption operation of the hydrogen by the hydrogen absorption and the emission ability, and the catalyst which carbon has essentially, it becomes possible [emitting sufficient quantity of hydrogen]. Moreover, the occlusion and emission of the hydrogen in low temperature (for example, room temperature) are possible for the hydrogen absorption ingredient of this invention, and since mixing of a hydrocarbon (HC) is prevented by the hydrogen desorption in this low temperature, the purity of the hydrogen emitted is excellently maintainable. Thus, the hydrogen absorption ingredient of this invention which has outstanding hydrogen absorption and emission ability can be obtained efficiently and certainly by the manufacture approach of this invention mentioned later.

[0027] That is, the manufacture approach of this invention includes the grinding process which obtains a graphite crystal grain child by mechanical grinding of a graphite, and the mixed process which mixes this graphite crystal grain child and the above-mentioned specific catalyst in a list. In addition, the manufacture approach of this invention concerned also includes the approach of mixing coincidence, i.e., the graphite which is not ground mechanically, and a catalyst for a grinding process and a mixed process, and performing mechanical grinding.

[0028] As for a grinding process, it is desirable to carry out so that the graphite crystal

grain child obtained may fulfill the conditions expressed with the above-mentioned formula (1), and, for this reason, the grinding equipments (ball mill etc.) which can be set up more than 2G are suitably used in grinding acceleration. When a planet ball mill is used especially, since the high grinding acceleration beyond 10G is obtained and the grinding effectiveness is heightened more, it is desirable.

[0029] Since it will be in the condition that the graphite under grinding tends to ignite if it faces performing a grinding process and oxygen exists in an ambient atmosphere, it is desirable to perform the grinding processing concerned under inert gas ambient atmospheres, such as an argon. Moreover, if grinding processing is performed under an inert gas ambient atmosphere, the amount of mixing of impurities, such as hydrogen and oxygen, can be reduced.

[0030] The graphite crystal grain child obtained at a grinding process is mixed with the above-mentioned specific catalyst, and the hydrogen absorption ingredient of this invention with which the catalyst concerned and carbon were fully distributed by homogeneity is obtained (mixed process).

[0031] In a mixed process, a catalyst may be mixed with a graphite crystal grain child as it is, and the predetermined compound which is the precursor of a catalyst may be mixed with a graphite crystal grain child, and a catalyst may be supported to a graphite crystal grain child. For example, when obtaining the hydrogen absorption ingredient with which platinum was supported by the graphite crystal grain child, platinum acetylacetonato can be used as a precursor of a catalyst.

[0032] Moreover, it is desirable to use supercritical fluid, such as a carbon dioxide (CO_2), as a solvent in the case of this mixed process. When a catalyst and carbon are mixed in supercritical fluid, it is in the inclination for both distributed homogeneity to improve and for hydrogen absorption and emission ability to be raised more. Although processing conditions change with classes of supercritical fluid at this time, 40-200 degrees C and a pressure are 5 - 50MPa, and 0.1 - 10 hours of the processing time are [the processing temperature in the case of using a carbon dioxide, for example] desirable respectively.

[0033] Although the hydrogen absorption ingredient of this invention which could carry out the homogeneity of a catalyst and the carbon fully minutely, and was excellent in hydrogen absorption and emission ability with an above-mentioned grinding process and an above-mentioned mixed process can be obtained efficiently and certainly, as for the manufacture approach of this invention, it is desirable that hydrogen down stream processing which contacts the hydrogen absorption ingredient obtained in hydrogen is included further. In having the active spot where the carbon contained in a hydrogen absorption ingredient causes irreversible reaction, there is a possibility that the hydrogen by which occlusion was once carried out may become that it is hard to be emitted at low temperature, but since termination of the active spot concerned is carried out and it is inactivated from hydrogen by performing this hydrogen down stream processing, the facilitatory effect of a reversible reaction (occlusion and emission of hydrogen) can be heightened more.

[0034] In case the hydrogen down stream processing concerned is performed, it is desirable respectively that processing temperature is 20-300 degrees C, and hydrogen pressure is 0.1-10MPa. For example, sufficient hydrogen processing is performed by holding the hydrogen absorption ingredient after a mixed process in 25 degrees C and the

ambient atmosphere of hydrogen pressure 5MPa.

[0035] Moreover, although the hydrogen down stream processing concerned may be performed once, the hydrogen absorption and emission ability of a hydrogen absorption ingredient can be raised more by performing this two or more times. That is, after making this hydrogen emit with reduced pressure etc., a hydrogen storage capacity (hydrogen burst size) can be made to increase by repeating the actuation to which hydrogen down stream processing is again carried out, and occlusion of the hydrogen is carried out, although occlusion of the hydrogen of the specified quantity is carried out to the hydrogen absorption ingredient after 1 time of hydrogen down stream processing.

[0036]

[Example] Hereafter, although this invention is explained still more concretely based on an example and the example of a comparison, this invention is not limited to the following examples at all.

[0037] In the glove compartment maintained at the [example 1] argon gas ambient atmosphere, graphite 5g was put into the container made from stainless steel (content volume: 80ml) with the stainless steel ball (4mmphi), and the planet ball mill performed mechanical grinding processing by 400rpm for 12 hours. Thereby, Raman full-width-at-half-maximum d of wave number 1350cm⁻¹ obtained by Raman spectrum measurement is 61cm⁻¹, the crystal grain child size La within the field containing the a-axis and b-axis of graphite structure is 3.7nm, and the graphite crystal grain child who fulfills the conditions expressed with the above-mentioned formula (1) was obtained.

[0038] Next, the carbon dioxide was enclosed and the container was sealed, after putting the obtained graphite crystal grain child into the reaction container made from stainless steel (content volume: 50ml) and adding platinum acetylacetonato 0.5g and acetone 5ml to this. With the oil bath, this reaction container was heated at 150 degrees C, and was held for 2 hours. The pressures in the reaction container at this time were 30MPa(s). Then, the inside of a reaction container was deaerated, the acetone and the carbon dioxide were removed, and the hydrogen absorption ingredient was obtained. When elemental analysis by ICP was performed about the obtained hydrogen absorption ingredient, the content rate of platinum was 11.2 % of the weight, and the content rate of the carbon on the basis of the total quantity of platinum and carbon was 99.2 atoms %.

[0039] Contents were moved to the reaction container made from stainless steel which can bear a vacuum and high pressure. This reaction container was connected to the exhauster and the inside of a reaction container was decompressed to 0.1Torr extent with the rotary pump. In order to perform degassing processing in a reaction container completely furthermore, under reduced pressure, it heated at 200 degrees C and held for 1 hour. Subsequently, when hydrogen (purity: it is the same as that of the following 99.999%) was introduced in the reaction container and it held to hydrogen pressure 5MPa at the room temperature (it is the same as that of 25 degrees C and the following), absorption of hydrogen was accepted immediately. After checking that absorption (fall of hydrogen pressure) of this hydrogen has stopped, the inside of a reaction container was decompressed at the room temperature, and hydrogen was made to emit.

[0040] Furthermore, the hydrogen desorption under a room temperature, the hydrogen absorption and the room temperature in hydrogen pressure 5MPa, and reduced pressure was repeated, and the burst size (the amount of occlusion) was calculated based on the hydrogen pressure in a container on the occasion of hydrogen desorption. Absorption and

emission of this hydrogen were repeated until the amount of hydrogen desorption reached constant value. Consequently, the amount of hydrogen desorption of the hydrogen absorption ingredient of this example showed 5.6 % of the weight of maximums.

[0041] The hydrogen absorption ingredient was produced like the example 1 except having used rhodium acetylacetonato instead of [example 2] platinum acetylacetonato. When ultimate analysis by ICP was performed about the obtained hydrogen absorption ingredient, the content rate of a rhodium was 13.8 % of the weight, and the content rate of the carbon on the basis of the total quantity of a rhodium and carbon was 98.2 atoms %.

[0042] Next, occlusion and emission of hydrogen were performed like the example 1 using the obtained hydrogen absorption ingredient. Consequently, the maximum of the amount of hydrogen desorption was 6.2 % of the weight.

[0043] In the glove compartment maintained at the [example 3] argon gas ambient atmosphere, graphite 5g and 1.0g (20-60mesh) of iron powder were put into the container made from stainless steel (content volume: 80ml) with the stainless steel ball (4mmphi), the planet ball mill performed mechanical grinding processing by 400 rotations for 12 hours, and the hydrogen absorption ingredient (the content rate of the carbon on the basis of the total quantity of iron and carbon: 96.5 atoms %) was obtained.

[0044] Next, occlusion and emission of hydrogen were performed like the example 1 using the obtained hydrogen absorption ingredient. Consequently, the maximum of the amount of hydrogen desorption was 5.1 % of the weight.

[0045] The hydrogen absorption ingredient was produced like the example 3 except having used magnesium dust (20-70mesh) instead of [example 1 of comparison] iron powder.

[0046] Next, occlusion and emission of hydrogen were performed like the example 1 using the obtained hydrogen absorption ingredient. Consequently, the maximum of the amount of hydrogen desorption is 0.3 % of the weight, and it was checked with the hydrogen absorption ingredient of this example of a comparison that the occlusion and emission of the hydrogen in a room temperature are difficult.

[0047]

[Effect of the Invention] Since the reversible reaction of the occlusion and emission of hydrogen is fully promoted by the synergistic effect of the hydrogen absorption and emission ability which carbon has essentially, and a desorption operation of the hydrogen by the above-mentioned specific catalyst, with the hydrogen absorption ingredient of this invention, it enables it to emit the hydrogen of a high grade and sufficient amount at low temperature, as explained above.

[0048] Moreover, according to the manufacture approach of this invention, when the particle diameter obtained according to a predetermined grinding process uses a detailed and uniform graphite crystal grain child as a carbonaceous raw material and mixes this with the above-mentioned specific catalyst, the hydrogen absorption ingredient of this invention which is excellent in hydrogen absorption and emission ability can be obtained efficiently and certainly.\\

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing typically an example of the graphite crystal particle concerning this invention.

[Description of Notations]

1 -- A carbon layer, La -- The crystal grain child size within the field containing the a-axis and b-axis of graphite structure, Lc -- Crystal grain child size of the direction of a c-axis of graphite structure.

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号
特開2003-165701
(P2003-165701A)

(43) 公開日 平成15年6月10日 (2003.6.10)

(51) Int. Cl.	識別記号	F I	テームト* (参考)
C 0 1 B 3/00		C 0 1 B 3/00	B 4 G 0 4 0
B 0 1 J 20/02		B 0 1 J 20/02	B 4 G 0 4 6
C 0 1 B 31/04	1 0 1	C 0 1 B 31/04	1 0 1 B 4 G 0 6 6

審査請求 未請求 請求項の数 5 O L (全 6 頁)

(21) 出願番号 特願2001-381155 (P2001-381155)

(22) 出願日 平成13年11月27日 (2001.11.27)

(71) 出願人 000003609

株式会社豊田中央研究所

愛知県愛知郡長久手町大字長湫字横道41番
地の1

(72) 発明者 若山 博昭

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内

(72) 発明者 福岡 啓幸

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内

(74) 代理人 100088155

弁理士 長谷川 芳樹 (外3名)

最終頁に続く

(54) 【発明の名称】 水素吸蔵材料及びその製造方法

(57) 【要約】

【課題】 高純度且つ十分な量の水素を低温で放出することができる水素吸蔵材料を提供すること。

【解決手段】 本発明の水素吸蔵材料は、ニッケル、クロム、モリブデン、コバルト、銅、パラジウム、白金、鉄、ルテニウム、ロジウム、イリジウム、タングステン、チタン、マンガン及びオスミウムからなる群より選ばれる少なくとも1種の触媒と、炭素とを含有することを特徴とする。

特開2003-165701

2

(2)

1

【特許請求の範囲】

【請求項1】 ニッケル、クロム、モリブデン、コバルト、銅、パラジウム、白金、鉄、ルテニウム、ロジウム、イリジウム、タングステン、チタン、マンガン及びオスミウムからなる群より選ばれる少なくとも1種の触媒と、炭素とを含有することを特徴とする水素吸蔵材料。

【請求項2】 前記炭素の原料として、ラマンスペクトル測定で得られる波数 1350 cm^{-1} のラマンピークの半値幅が下記式(1)：

$$d < (376/La) + 19.0 \quad (1)$$

【式中、 d はラマンピークの半値幅(cm^{-1})を表し、 La は黒鉛構造の a 軸及び b 軸を含む面内の結晶粒子サイズ(nm)を表す】で表される条件を満たす黒鉛結晶粒子を配合してなるものであることを特徴とする。請求項1に記載の水素吸蔵材料。

【請求項3】 前記炭素の含有割合が、前記触媒と前記炭素との合計量を基準として40原子%以上であることを特徴とする。請求項1又は2に記載の水素吸蔵材料。

【請求項4】 黒鉛の機械的粉碎により黒鉛結晶粒子を得る粉碎工程と、前記粉碎工程で得られる黒鉛結晶粒子と、ニッケル、クロム、モリブデン、コバルト、銅、パラジウム、白金、鉄、ルテニウム、ロジウム、イリジウム、タングステン、チタン、マンガン及びオスミウムからなる群より選ばれる少なくとも1種の触媒とを混合して、該触媒と炭素とを含有する水素吸蔵材料を得る混合工程と、を含むことを特徴とする水素吸蔵材料の製造方法。

【請求項5】 前記水素吸蔵材料を水素と接触させる水素処理工程をさらに含むことを特徴とする。請求項4に記載の水素吸蔵材料の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、水素吸蔵材料及びその製造方法に関する。

【0002】

【従来の技術】 現代社会において、水素は合成化学工業や石油精製などに多量に利用されている重要な化学原料である。一方、将来におけるエネルギー問題や環境問題を解決するために、クリーンなエネルギーとしての水素

【0004】 一方、水素の貯蔵法としては、圧縮してボンベに貯蔵する方法、冷却して液体水素とする方法、活性炭に吸着させる方法、水素吸蔵材料を利用する方法などが提案されている。これらの方法の中でも、水素吸蔵材料を利用する方法は燃料電池自動車などの移動媒体において主要な役割を果たすと考えられている。

【0005】 このような背景の下、水素吸蔵材料としての炭素の使用が提案されている（特表平8-504394号公報、特開2000-103612号公報、特開2001-106516号公報など）。また、特開2000-87172号公報には、従来より水素吸蔵材料として検討が進められているアルカリ土類金属（ Mg 、 Ca など）に炭素を混合した水素吸蔵材料が開示されており、かかるアルカリ土類金属と炭素との混合によりアルカリ土類金属の水素化速度の向上が図られている。さらに、 Mg とグラファイトからなる水素吸蔵材料を製造する際に、得られる水素吸蔵材料の特性の向上を目的として、特定の有機化合物（ THF など）の共存下で機械的粉碎を行う方法が提案されている（J. Alloys. Compd. 293-295 (1999) p564-568, Chem. Commun. (1999) p2277-2278など）。

【0006】

【発明が解決しようとする課題】 しかしながら、上記従来の水素吸蔵材料であっても、単位重量当たりの水素吸蔵量が必ずしも多いものではなく、実用化の点で十分な水素吸蔵・放出能を有しているとは言い難い。また、水素吸蔵材料には水素の吸蔵・放出を低温（好ましくは室温）で可逆的に行えることが望まれるが、上記従来の水素吸蔵材料から水素を放出させるためには高温（例えば 500°C 以上）に加熱する必要がある。かかる加熱により放出される水素中に炭化水素（ HC ）が混入しやすくなって水素の純度が不十分となる。

【0007】 本発明は、上記従来技術の有する課題に鑑みてなされたものであり、高純度且つ十分な量の水素を低温で放出することができると水素吸蔵材料を提供することを目的とする。

【0008】

【課題を解決するための手段】 上記課題を解決するために、本発明の水素吸蔵材料は、ニッケル、クロム、モリブデン、コバルト、銅、パラジウム、白金、鉄、ルテニ

(3)

特開2003-165701

3

料として、ラマンスペクトル測定で得られる波数1350 cm⁻¹のラマンピークの半値幅が下記式(1)：

$$d < (376/La) + 19.0 \quad (1)$$

【式中、dはラマンピークの半値幅(cm⁻¹)を表し、Laは黒鉛構造のa軸及びb軸を含む面内の結晶粒子サイズ(nm)を表す】で表される条件を満たす黒鉛結晶粒子を配合してなるものであることが好ましい。上記特定の条件を満たす黒鉛結晶粒子を触媒に配合すると、触媒と炭素との分散均一性の向上により上記の相乗効果がより高められるので、より優れた水素吸蔵・放出能を有する水素吸蔵材料が実現される。

【0011】また、本発明の水素吸蔵材料においては、炭素の含有割合が、触媒と炭素との合計量を基準として40原子%以上であることが好ましい。炭素の含有割合が40原子%以上であると、水素吸蔵・放出能がより向上する傾向にある。

【0012】また、本発明の水素吸蔵材料の製造方法は、黒鉛の機械的粉碎により黒鉛結晶粒子を得る粉碎工程と、粉碎工程で得られる黒鉛結晶粒子と、ニッケル、クロム、モリブデン、コバルト、銅、パラジウム、白金、鉄、ルテニウム、ロジウム、イリジウム、タンゲステン、チタン、マンガン及びオスミウムからなる群より選ばれた少なくとも1種の触媒とを混合して、該触媒と炭素とを含有する水素吸蔵材料を得る混合工程と、を含むことを特徴とする。

【0013】本発明の製造方法によれば、かかる粉碎工程により粒子径が微細且つ均一な黒鉛結晶粒子が得られる。かかる黒鉛結晶粒子を炭素の原料とし、これを上記特定の触媒と混合することによって、水素吸蔵・放出能に優れた本発明の水素吸蔵材料を効率よく且つ簡便に得ることができる。

【0014】本発明の製造方法は、水素吸蔵材料を水素と接触させる水素処理工程をさらに含むことが好ましい。水素吸蔵材料に含まれる炭素が不可逆反応の原因となる活性点を有する場合には、一旦吸蔵された水素が低温で放出されにくくなるおそれがあるが、かかる水素処理工程を行うことによって、当該活性点が水素で終端されて不活性化されるので、可逆反応(水素の吸蔵・放出)の促進効果をより高めることができる。

【0015】

4

の脱離作用を得ることができる。これらの触媒は、1種を単独で用いてもよく、2種以上を組み合わせてもよい。

【0017】当該触媒の形状は特に制限されないが、その平均粒径は10μm以下であることが好ましい。平均粒径が10μm以下の触媒を用いることによって、当該触媒と炭素との接触効率が増加するので、炭素が本来的に有する水素吸蔵放出能と触媒の脱水素作用との相乗効果をより高めることができる。

【0018】本発明の水素吸蔵材料は、上記の触媒と炭素とを含んで構成される。かかる炭素の原料としては、純度の高い天然黒鉛や、高配向性熱分解黒鉛(HOPG)のような黒鉛化度の高い人造黒鉛などの黒鉛(グラファイト)を用いることが好ましい。

【0019】図1は本発明で用いられる黒鉛結晶粒子の一例を模式的に示す説明図である。図1において、ほぼ同じ形状、面積を有する炭素層1がカラム状に積層して黒鉛構造の結晶粒子が構成されている。また、図1中、La[nm]は黒鉛構造のa軸及びb軸を含む面内の結晶粒子サイズ(炭素層1の面に水平な方向における結晶粒子径)、Lc[nm]は黒鉛構造のc軸方向の結晶粒子サイズ(炭素層1の積み重なるの厚さ)を表す。

【0020】当該黒鉛結晶微粒子としては、結晶性及び結晶粒子径の均一性が高いものを用いることが好ましく、具体的には、ラマンスペクトル測定で得られる波数1350 cm⁻¹のラマンピークの半値幅dと結晶粒子サイズLaとが下記式(1)：

$$d < (376/La) + 19.0 \quad (1)$$

で表される条件を満たす黒鉛結晶粒子を用いることが好ましい。上記式(1)で表されるdとLaとの関係は炭素の結晶性及び結晶粒子径の均一性の指標であり、dとLaとが上記の条件を満たさない場合には、結晶性及び結晶粒子径の均一性が低く水素吸蔵・放出能が不十分となる傾向にある。また、上記と同様の理由により、半値幅dと結晶粒子サイズLaとが下記式(2)：

$$d < (341/La) + 10.5 \quad (2)$$

で表される条件を満たす黒鉛結晶粒子を用いることがより好ましい。

【0021】また、当該黒鉛結晶粒子においては、結晶粒子サイズLaが4.0nm以下であることが好まし、

(4)

特開2003-165701

5

【0023】また、当該黒鉛結晶粒子において、炭素と水素との原子数の比(H/C)は0.05以下であることが好ましい。H/Cが0.05以下であると、結晶粒子の末端における水酸基やカルボキシル基などの形成が抑制される。

【0024】本発明の水素吸蔵材料において、触媒と炭素との接触が十分であればこれらの分散状態は特に制限されない。例えば、触媒粒子と黒鉛結晶粒子とが微細に分散している状態、黒鉛結晶粒子の炭素層の層間に触媒粒子が導入されて層間化合物が形成された状態、あるいは触媒粒子が黒鉛結晶粒子表面に担持された状態のいずれであってもよい。また、例えば炭素原料として上記式

(1)で表される条件を満たす黒鉛結晶粒子を用いた場合、当該黒鉛結晶粒子は水素吸蔵材料中で式(1)で表される条件を満たさない状態で分散されていてもよい。

【0025】また、触媒及び炭素の含有割合は、十分な水素吸蔵・放出能が得られる限りにおいて特に制限されないが、炭素の含有割合が、触媒と炭素との合計量を基準として40原子%以上であることが好ましい。炭素の含有割合が40原子%未満であると水素吸蔵・放出能が低下する傾向にある。

【0026】このように本発明の水素吸蔵材料は、上記特定の触媒と炭素とを含有するものであり、炭素が本来的に有する水素吸蔵・放出能と触媒による水素の脱離作用との相乗効果により水素の吸蔵・放出の可逆反応が十分に促進されるので、十分な量の水素を放出することが可能となる。また、本発明の水素吸蔵材料は、低温(例えば室温)での水素の吸蔵・放出が可能なるものであり、かかる低温での水素放出により炭化水素(HC)の混入が防止されるため、放出される水素の純度を高水準に維持することができる。このように優れた水素吸蔵・放出能を有する本発明の水素吸蔵材料は、後述する本発明の製造方法により効率よく且つ確実に得ることができる。

【0027】すなわち、本発明の製造方法は、黒鉛の機械的粉碎により黒鉛結晶粒子を得る粉碎工程、並びに該黒鉛結晶粒子と上記特定の触媒とを混合する混合工程を含むものである。なお、当該本発明の製造方法は、粉碎工程と混合工程とを同時に、すなわち機械的に粉碎されずに黒鉛と触媒とを混合して機械的粉碎を行う方法をも包含するものである。

5

砕処理を行うと、水素、酸素などの不純物の混入量を低減することができる。

【0030】粉碎工程で得られる黒鉛結晶粒子は上記特定の触媒と混合され、当該触媒と炭素とが十分に均一に分散された本発明の水素吸蔵材料が得られる(混合工程)。

【0031】混合工程においては、触媒をそのまま黒鉛結晶粒子と混合してもよく、また、触媒の前駆体である所定の化合物を黒鉛結晶粒子と混合して触媒を黒鉛結晶粒子に担持してもよい。例えば黒鉛結晶粒子に白金が担持された水素吸蔵材料を得る場合には、触媒の前駆体として白金アセチルアセトナートを用いることができる。

【0032】また、かかる混合工程の際には、溶媒として二酸化炭素(CO₂)などの超臨界流体を用いることが好ましい。超臨界流体中で触媒と炭素とを混合すると、両者の分散均一性が向上して水素吸蔵・放出能がより高められる傾向にある。このとき、処理条件は超臨界流体の種類により異なるが、例えば二酸化炭素を用いる場合の処理温度は40~200℃、圧力は5~50MPa、処理時間は0.1~10時間がそれぞれ好ましい。

【0033】上記の粉碎工程及び混合工程により、触媒と炭素とを十分に微細に且つ均一にすることができ、水素吸蔵・放出能に優れた本発明の水素吸蔵材料を効率よく且つ確実に得ることができるが、本発明の製造方法は、得られる水素吸蔵材料を水素と接触させる水素処理工程をさらに含むことが好ましい。水素吸蔵材料に含まれる炭素が不可逆反応の原因となる活性点を有する場合には、一旦吸蔵された水素が低温で放出されにくくなるおそれがあるが、かかる水素処理工程を行うことによって、当該活性点が水素で終端されて不活性化されるので、可逆反応(水素の吸蔵・放出)の促進効果をより高めることができる。

【0034】当該水素処理工程を行う際には、処理温度が20~300℃、水素圧が0.1~10MPaであることがそれぞれ好ましい。例えば、混合工程後の水素吸蔵材料を25℃、水素圧5MPaの雰囲気中に保持することにより十分な水素処理が施される。

【0035】また、当該水素処理工程は1回のみ行ってもよいが、これを複数回行うことによって水素吸蔵材料の水素吸蔵・放出能をより高めることができる。すなわ

特開2003-165701

8

(5)

7

たグローブボックス内で、グラファイト5gをステンレス球(4mmφ)と共にステンレス製容器(内容積:80ml)に入れ、遊星ボールミルにて400rpmで12時間機械的粉碎処理を行った。これにより、ラマンスペクトル測定で得られる波数 1350 cm^{-1} のラマンピークの半値幅 d が 61 cm^{-1} であり、黒鉛構造のa軸及びb軸を含む面内の結晶粒子サイズ L_a が3.7nmであり、上記式(1)で表される条件を満たす黒鉛結晶粒子を得た。

【0038】次に、得られた黒鉛結晶粒子をステンレス製反応容器(内容積:50ml)に入れ、これに白金アセチルアセトナート0.5g及びアセトン5mlを加えた後、二酸化炭素を封入して容器を密閉した。この反応容器をオイルバスで 150°C に加熱して2時間保持した。このときの反応容器内の圧力は30MPaであった。その後、反応容器内を脱気してアセトン及び二酸化炭素を除去して水素吸蔵材料を得た。得られた水素吸蔵材料についてICPによる元素分析を行ったところ、白金の含有割合は11.2重量%であり、白金と炭素との合計量を基準とした炭素の含有割合は99.2原子%であった。

【0039】内容物を真空且つ高圧に耐え得るステンレス製反応容器に移した。この反応容器を排気装置に接続し、ロータリーポンプにより反応容器内を0.1Torr程度まで減圧した。さらに反応容器内の脱気処理を完全に行うために、減圧下で 200°C に加熱して1時間保持した。次いで、室温(25°C 、以下同様である)にて、水素(純度:99.999%、以下同様である)を反応容器内に導入して水素圧5MPaに保持したところ、直ちに水素の吸収が認められた。この水素の吸収(水素圧の低下)が停止したことを確認した後、室温で反応容器内を減圧して水素を放出させた。

【0040】さらに、室温、水素圧5MPaでの水素吸収と室温、減圧下での水素放出とを繰り返す、水素放出の際にはその放出量(吸蔵量)を容器内の水素圧に基づいて求めた。この水素の吸収・放出を水素放出量が一定値に達するまで繰り返した。その結果、本実施例の水素吸蔵材料の水素放出量は最大値5.6重量%を示した。

【0041】【実施例2】白金アセチルアセトナートの代わりにロジウムアセチルアセトナートを用いたことと

り、ロジウムと炭素との合計量を基準とした炭素の含有割合は98.2原子%であった。

【0042】次に、得られた水素吸蔵材料を用い、実施例1と同様にして水素の吸蔵・放出を行った。その結果、水素放出量の最大値は6.2重量%であった。

【0043】【実施例3】アルゴンガス雰囲気になれたグローブボックス内で、グラファイト5g及び鉄粉(20-60mesh)1.0gをステンレス球(4mmφ)と共にステンレス製容器(内容積:80ml)に入れ、遊星ボールミルにて400回転で12時間機械的粉碎処理を行って、水素吸蔵材料(鉄と炭素との合計量を基準とした炭素の含有割合:96.5原子%)を得た。

【0044】次に、得られた水素吸蔵材料を用い、実施例1と同様にして水素の吸蔵・放出を行った。その結果、水素放出量の最大値は5.1重量%であった。

【0045】【比較例1】鉄粉の代わりにマグネシウム粉末(20-70mesh)を用いたこと以外は実施例3と同様にして水素吸蔵材料を作製した。

【0046】次に、得られた水素吸蔵材料を用い、実施例1と同様にして水素の吸蔵・放出を行った。その結果、水素放出量の最大値は0.3重量%であり、本比較例の水素吸蔵材料では室温での水素の吸蔵・放出が困難であることが確認された。

【0047】

【発明の効果】以上説明した通り、本発明の水素吸蔵材料では、炭素が本来的に有する水素吸蔵・放出能と上記特定の触媒による水素の脱離作用との相乗効果によって、水素の吸蔵・放出の可逆反応が十分に促進されるので、高純度且つ十分な量の水素を低温で放出することが可能となる。

【0048】また、本発明の製造方法によれば、所定の粉碎工程により得られる粒子径が微細且つ均一な黒鉛結晶粒子を炭素の原料とし、これを上記特定の触媒と混合することによって、水素吸蔵・放出能に優れる本発明の水素吸蔵材料を効率よく且つ確実を得ることができる。

【図面の簡単な説明】

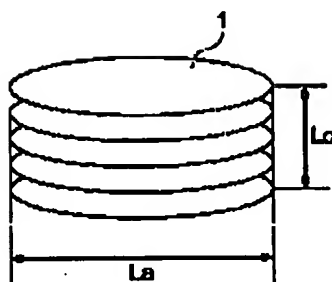
【図1】本発明にかかる黒鉛結晶微粒子の一例を模式的に示す説明図である。

【符号の説明】

(5)

特開2003-165701

【図1】



フロントページの続き

Fターム(参考) 4G040 AA34 AA36 AA42
4G046 EA05 EB13 EC02 EC05
4G056 AA02D AA04B BA38 CA38
FA40 CA14

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.